Asian Journal of Chemistry Vol. 4, No. 2 (1992), 257–262

Spectrophotometric Determination of Cobalt and Palladium After Extraction of their n-Amylthioglycolate Complexes into Chloroform

ASHOK KUMAR MALIK, USHA GUPTA and A. L. J. RAO*

Department of Chemistry, Punjabi University
Patiala–147 002, India

Cobalt and palladium react quantitatively with *n*-amylthioglycolate (ATG) to form water insoluble coloured complexes in the pH range 8.0–10.0 and 4.0–8.0, respectively. As the equilibrium is established rapidly, these complexes can be extracted into chloroform. The colour of the complexes is quite stable. The pink coloured cobalt complex has λ_{max} at 500 nm while the yellow coloured palladium complex absorbs maximum at 380 nm. Beer's law is obeyed over the concentration ranges 0.092–0.825 ppm and 0.50–4.93 ppm, for cobalt and palladium, respectively. The molar absorptivities and Sandell's sensitivities for the two complexes are 3.2×10^4 1 mol^{-1} cm^{-1} and 0.73×10^4 1 mol^{-1} cm^{-1}, and 0.00164 μg Co cm^{-2} and 0.0145 μg Pd cm^{-2}, respectively. Then replicate determinations on sample solution containing 5.9 μg of cobalt and 43.5 μg of palladium gave mean absorbance 0.32 and 0.30, with relative standard deviations of 3.09% and 3.05%.

INTRODUCTION

Although there are many methods involving organic complexing reagents for the determination of cobalt and palladium[1–7]. Most of these are time consuming, less sensitive and require preparation of the interfering ions. The nitroso-*R* salt[8,9] methods require rigid control of pH, reagent concentration and duration of boiling. In the present study, we present a rapid, more sensitive, selective, and reliable spectrophotometric method for the determination of these metals, using *n*-amylthioglycolate as the complexing reagent. Various parameters involved in the extraction have been studied in detail and the method has been applied for the determination of these metals in synthetic samples and in alloys.

EXPERIMENTAL

A Spectronic 20-Spectrophotometer for measuring the absorbance and ECIL digital pH meter were used. All solvents and reagents were of analytical reagent grade unless stated otherwise.

n-Amylthioglycolate was synthesised by the method of Gambarov[10]. Thioglycolic acid (1 mol) was mixed with *n*-amyl alcohol (5 mol), cooled, stirred and saturated with hydrogen chloride and then held at 80–90°C for 8–12 hrs. The reaction mixture was extracted with benzene and washed with water. Benzene was removed by distillation under reduced prcssure. The product has the following characteristics: density ($d_{35°}$) 0.81174 g 1^{-1}; b. pt. 138–139°C. The results of elemental analysis were in

good agreement with theoretical composition $C_7H_{14}O_2S$. A 0.1% solution of ATG was prepared in ethanol and standardised titrimetrically using mercury(II) acetate as titrant and diphenylcarbazone as the internal indicator. Stock solutions (0.01 M cobalt and 0.001 M palladium) were prepared in double distilled acidulated water from their analytical reagent grade samples and standardised by known methods. Solutions of lower concentration were subsequently prepared by appropriate dilutions of the stock solutions.

General Procedure

Add 1.0 ml of the reagent solution (0.1%) to aliquots of the metal ion solutions. Adjust pH to 5.5 for palladium and 9.5 for cobalt and then add 2.0 ml of appropriate buffer and enough potassium chloride solution to give 0.1 M concentration after dilution to 10 ml (which facilitates the extraction) of the final solution. Transfer the solutions into separating funnels containing 10 ml of chloroform and shake the resulting mixture for 2 mins. Allow the phases to separate and pour the organic layer over 2 g of calcium chloride to dehydrate. Measure absorbance at 500 nm for cobalt and at 380 nm for palladium against reagent blanks prepared under similar conditions.

RESULTS AND DISCUSSION

Absorption spectra of ATG and its cobalt and palladium complexes in chloroform were recorded against ethanol and reagent blank, respectively. The cobalt and palladium complexes show an absorption maximum at 510 nm and 380 nm respectively. The extractions were found to be quantitative with 0.8–1.0 ml of the reagent solution (higher amounts in case of cobalt cause decrease in the absorbance) at pH 8.0–10.0 for cobalt and 4.0–8.0 for palladium. The effect of the presence of sodium acetate, potassium chloride and potassium nitrate on extraction was studied. The absorbance was maximum 0.04–1.0 M at concentration. In the absence of electrolyte the extraction was incomplete. Various solvents such as benzene, toluene, carbon tetrachloride, ethyl acetate, 1,2-dichloromethane, diethyl ether, isobutyl methyl ketone, butyl acetate and chloroform were examined for the extraction of these complexes. Chloroform was found to be the most effective. With 10 ml of chloroform the complexes were recovered to the extent of 99.99% in a single extraction. Whereas with other solvents extractions were incomplete. For the complete extraction shaking time of 2 min was found to be adequate. The complexes were stable for more than 8 hrs in the extract. Job's method of continous variation and mole ratio method were employed to establish the composition of these complexes. The results indicated that 1 : 2 complexes are formed by cobalt and

palladium thus suggesting the extraction of $Co(C_7H_{13}O_2S)_2$ and $Pd(C_7H_{13}O_2S)_2$.

Beer's Law and Sensitivity

Beer's law holds over the concentration ranges 0.092–0.825 ppm for cobalt and 0.50–4.93 ppm for palladium, respectively. The slopes of calibration curves are calculated to be 0.542 ml μg^{-1} for cobalt and 0.069 ml μg^{-1} for palladium. The molar absorptivities and Sandell's sensitivities are calculated to be 3.2×10^4 l mol^{-1} cm^{-1} and 0.00164 μg Co cm^{-2} for cobalt and 0.73×10^4 l mol^{-1} cm^{-1} 0.0145 μg Pd cm^{-2} for palladium. Ten replicate determinations on sample solutions containing 5.9 μg of cobalt and 43.5 μg of palladium in 10 ml of final solution, gave mean absorbances of 0.32 and 0.30, with relative standard deviation of 3.09% and 3.05% respectively. The limit of detection are calculated to be 0.033 ppm and 0.4 ppm, respectively, for cobalt and palladium, according to IUPAC's definition[11].

Effect of Diverse Ions

The interference of various ions was studied in detail. The different ions were added individually to aliquots containing 5.9 μg of cobalt and 43.5 μg of palladium and the extractions carried out. Among the anions examined (Table 1) for cobalt and palladium, results were low in the

TABLE 1
EFFECT OF DIVERSE ANIONS ON THE DETERMINATION OF COBALT AND PALLADIUM. Co : 5.9 μg, pH : 9.5; Pd : 43.5 μg, pH 5.5; n-AMYLTHIOGLYCOLATE (0.1%) : 1.0 ml

Salt added	Amount of anion added (mg)	Absorbance* for	
		Cobalt at 500 nm	Palladium at 380 nm
	—	0.32	0.30
Acetate	20	0.32	0.30
Bromide	20	0.32	0.30
Chloride	20	0.32	0.30
Fluoride	20	0.32	0.30
Citrate	20	0.32	0.30
Iodide	20	0.32	0.30
Thiocaynate	20	0.32	0.30
Tartarate	20	0.32	0.30
Oxalate	20	0.32	0.30
Nitrate	20	0.32	0.30
Sulphate	20	0.32	0.30
Sulphite	10	0.32	0.30
Phosphate	05	0.32	0.30
Thiosulphate	01	0.32	0.30
EDTA	Interfered strongly.		

*Average of three determinations.

presence of phosphate, citrate and sulphate. EDTA interfered strongly in the determination. Of the cations examined (Table 2), Al(III), Bi(III),

TABLE 2

EFFECT OF DIVERSE CATIONS ON THE DETERMINATION OF COBALT AND PALLADIUM CONDITIONS SAME AS IN TABLE 1

Metal salt added	Amount of cation added (mg)	Absorbance* for	
		Cobalt at 500 nm	Palladium at 380 nm
	—	0.32	0.30
Al(III)	1.0	0.32	0.30
Mn(II)	1.0	0.32	0.30
U(VI)	1.0	0.32	0.30
Os(VIII)	1.0	0.32	0.30
Pt(IV)	0.5	0.32	0.30
Cd(II)	1.0	0.32	0.30
Zn(II)	1.0	0.32	0.30
Pb(II)	1.0	0.32	0.30
Bi(III)	1.0	0.32	0.30
Pd(II)*	1.0	0.32	—
Fe(III)**	1.0	0.32	0.30
Mo(VI)	1.0	0.32	0.30
In(IV)	1.0	0.32	0.30
Cu(II)	0.5	0.32	0.30
Rh(III)	0.5	0.32	0.30
Ni(II)***	1.0	0.32	0.30

*Separated by pre-extraction at low pH.
**Masked with 2.0 ml of 5% NaF.
***Interference was removed by decomposing the nickel complex with 2–4 M HCl.

In(III), Mn(III), Pt(IV), Os(VIII), U(VI), Mo(VI), Cu(II) and Ag(I) did not interfere. Presence of low amounts of Pb(II), Zn(II) and Cd(II) are tolerable.

Determination of Cobalt in Alloys

The alloy sample (0.1–0.5 g) was taken in a beaker to which were added 10–20 ml of aqua-regia. The solution was evaporated, till almost dry. Another 10 ml of concentrated hydrochloric acid was added and the solution was diluted, filtered and made up to 500 ml in a standard flask. An aliquot of this solution was taken, to which 1.5 ml of ATG (0.1%) was added. The nickel complex was destroyed by heating with 2–4 M hydrochloric acid, nitric acid or perchloric acid and iron was masked with 5%

sodium fluoride and cobalt was determined by the general procedure. Results are given in Table 3.

Determination of Palladium in Synthetic Samples

Different amounts of metal salts including that of palladium were mixed in such a way that the resultant mixtures were corresponded to some standard reference alloy. The mixture (0.2–0.3 g) was completely dissolved

TABLE 3

DETERMINATION OF COBALT AND PALLADIUM IN SOME ALLOYS AND SYNTHETIC SAMPLES

Name of alloy	Certificated %, composition of alloy	Amount of metal taken (μg)	Amount of metal; found (μg)	Average (μg)	Error %
Eligiloy	Co : 40.00 Ni : 15.00 Mn : 02.00 Cr : 20.00 Mo : 07.00 Fe* : 15.00 Be : 0.05 C : 00.15	Co : 4.00	3.90 4.10 4.05 4.00 4.10	4.03	0.75
High speed steel	Co : 9.25 Mn : 0.04 SI : 0.35 S : 0.05 P : 0.05 Cr : 4.15 Mo : 5.50 W : 6.0–8.0 Rest iron*	Co : 8.0	8.00 8.15 7.90 8.10 8.10	8.05	0.62
Platinum -iridium alloy	Pd : 03.50 Pb : 55.00 Pd : 14.90 Ir : 28.00 Rh : 07.00 Cu : 03.00 Fe* : 03.50	Pd : 14.90	14.90 14.95 14.92 14.93 14.95	14.93	0.20
Oakay alloy	Pd : 03.50 Pb : 60.00 Pt : 20.00 V : 09.50	Pd : 32.92	32.90 32.92 32.88 32.90 32.82	32.82	0.3

*Masked with 2.0 ml of 5% NaF.

in 25–30 ml of aqua-regia and the solution was evaporated to about 5 ml. Concentrated hydrochloric acid (10 ml) being added to it the solution was warmed. After cooling to room temperature, it was diluted to 500 ml in standard flask. To an aliquot of this sample solution was added 2.0 ml of 5% sodium fluoride in order to mask iron. The determination of palladium was then carried out by the general procedure. The results are given in Table 3.

REFERENCES

1. D. M. Smith and J. R. Hayes, *Anal. Chem.*, **31**, 898 (1959).
2. J. A. Dalziel and A. K. Stawinski., *Talanta*, **19**, 1190 (1972).
3. W. D. Jacobs and J. H. Yoe, *Anal. Chim. Acta.* **20**, 332 (1959).
4. P. K. Paria and S. K. Majumdar, *Indian J. Chem.*, **24**, 629 (1985).
5. D. G. Gambarov A. M. Ayubova, and S. R. Azimova, *Azerb. Khim. Zh.*, **12**, 122 (1981); *Chem. Abstr.*, **96**, 154569m (1982).
6. K. D. Dutta and J. Das, *J. Indian Chem. Soc.*, **52**, 1026 (1975).
7. A. Kumar, M. F. Hussain, M. Satake and B. K. Puri, *Bull. Chem. Soc. Jpn.*, **55**, 1455 (1982).
8. L. A. Bakhmutov, *Zav. Lab.*, **22**, 1321 (1956); *Chem. Abstr.*, **51**, 11164 (1957).
9. R. S. Young, E. T. Pinkey and R. Dick, *Ind. Eng. Chem. Anal. Ed.*, **18**, 474 (1945).
10. D. G. Gambarov, K. Z. Guseinov and Fati-Zade, *R. Org. Reagentry, Anal. Khim. Tezisy Dokl. Vses Konf. 4th*, **1**, 111 (1976); *Chem, Abstr.*, **87**, 193132 p. (1977).
11. G. L. Long and J. D. Winefordner, *Anal. Chem.*, **55**, 712A (1983).

[*Received*: 26 April 1990, *Accepted*: 10 February 1991] AJC-262